SECTION THREE Methods

This section describes the field and laboratory methods used to implement the Monitoring Program, which includes precipitation and flow monitoring, storm water sampling, and laboratory analyses.

3.1 PRECIPITATION AND FLOW MEASUREMENT

3.1.1 Precipitation Monitoring

For every monitoring station, a minimum of one automatic tipping bucket (intensity measuring) rain gage is located nearby or within the tributary watershed. Large watersheds may require multiple rain gages to accurately characterize the rainfall. The LACDPW operates various automatic rain gages throughout the county. Existing gages near the monitored watersheds are also utilized in calculating storm water runoff and are essential to develop runoff characteristics for these watersheds.

3.1.2 Flow Monitoring

Flow monitoring equipment is needed to trigger the automated samplers because the Monitoring Program requires flow-weighted composites for many constituents. Flows are determined from measurements of water elevation as described below.

The water elevation in a storm drain is measured by the stage monitoring equipment, and the flow rate is derived from a previously established rating table for the site or calculated with an equation such as Manning's. The LACDPW uses rating tables generated from analysis of storm drain cross sections and upstream/downstream flow characteristics. The rating tables are modified if it is demonstrated in the field through stream velocity measurements that calculated table values are incorrect. Previous storm water flow measurement efforts indicates that all stations will require multiple storm events to gather the data necessary for calibration of the measurement devices.

The automatic samplers utilize pressure transducers as the stage measurement device. However, pressure transducers are only accurate as flow measurement devices in open channel flow regimes. Therefore, for stations monitoring flows in underground storm drains, efforts were made to select drains that do not surcharge (flow under pressure) during events smaller than a 10-year storm event.

3.2 STORM WATER SAMPLING

3.2.1 Sample Collection Methods

Grab and composite sample collection methods, defined below, were used during the 2002-2003 storm season.

• **Grab Sample** - a discrete, individual sample taken within a short period of time, usually less than 15 minutes. This method is used to collect samples for constituents that have very short

holding times and specific collection or preservation needs. For example, samples for coliforms are taken directly into a sterile container to avoid non-resident bacterial contamination

• Composite Sample - a mixed or combined sample created by combining a series of discrete samples (aliquots) of specific volume, collected at specific flow-volume intervals. Composite sampling is ideally conducted over the duration of the storm event.

During a storm event, grab samples were collected during the initial portion of the storm (on the rising limb of the hydrograph) and taken directly to the laboratory.

Flow composite storm samples were obtained using an automated sampler to collect samples at flow-paced intervals. Samples collected at each station were combined in the laboratory to create a single flow-weighted sample for analysis.

During the storm season, the sampler was programmed to start automatically when the water level in the channel or storm drain exceeded the maximum annual dry weather stage. A sample was collected each time a set volume of water had passed the monitoring point (this volume is referred to as the pacing volume or trigger volume). The sample was stored in glass containers within the refrigerated sampler. A minimum of eight liters of sample was required to conduct the necessary laboratory analyses for all the constituents. The automated sampler was deactivated by field personnel when the water level in the channel or storm drain fell to about 120 percent of the observed maximum annual dry weather flow stage.

Samples were retrieved from the automated samplers as soon as possible to meet laboratory analysis holding time requirements. As samples were collected, rainfall and runoff data were logged and stored for transfer to the office.

3.2.2 Field Quality Assurance/Quality Control Plan

Properly performed monitoring station set up, water sample collection, sample transport, and laboratory analyses are vital to the collection of accurate data. Quality Assurance/Quality Control (QA/QC) is an essential component of the monitoring program.

Evaluation of Analytes and QA/QC Specifications for Monitoring Program (Woodward-Clyde, 1996a) describes the procedures used for bottle labeling, chain-of-custody tracking, sampler equipment checkout and setup, sample collection, field blanks to assess field contamination, field duplicate samples, and transportation to the laboratory.

An important part of the QA/QC Plan is the continued education of all field personnel. Field personnel were adequately trained from the onset and informed about new information on storm water sampling techniques on a continuing basis. Field personnel also evaluate the field activities required by the QA/QC Plan, and the Plan is updated if necessary.

Bottle Preparation

For each monitoring station, a minimum of three sets of bottles was available so that up to two complete bottle change-outs could be made for each storm event. Bottle labels contained the following information:

• LACDPW Sample ID Number

- Station Number
- Station Name
- Sample Type (Grab or Composite)
- Laboratory Analysis Requested
- Date
- Time
- Preservative
- Temperature
- Sampler's Name

Bottles were cleaned at the laboratory prior to use, then they were labeled and stored in sets. Each station was provided with the same number, types, and volumes of bottles for each rotation unless special grab samples were required. Clean composite sample bottles were placed in the automated sampler when samples were collected. This practice ensured readiness for the next storm event. All bottles currently not in use were stored and later transported in plastic ice chests. Composite sample bottles were limited to a maximum of 2-1/2 gallons each, to ensure ease of handling.

Chain-of-Custody Procedure

Chain-of-custody forms were completed to ensure and document sample integrity. These procedures establish a written record which tracks sample possession from collection through analysis.

Field Setup Procedures

All field sampling locations were fixed sites, with the sampler placed on a public road or flood control right-of-way. After sample collection, field staff prepared the sampler for collection of the next set of samples either in storm mode or in dry weather mode. Inspection of visible hoses and cables was performed to ensure proper working conditions according to the site design. Inspection of the strainer, pressure transducer, and auxiliary pump was performed during daylight hours in non-storm conditions.

The automated sampler was checked at the beginning of the storm (during grab sample collection) to ensure proper working condition and to see if flow composite samples were being collected properly. Dry weather collection techniques were similar, with grab and 24-hour composite samples being collected.

Bottles were collected after each event and packed with ice and foam insulation inside individually marked ice chests. Chain-of-custody forms were completed by field staff before transportation of the samples to the laboratory. Under no circumstance were samples removed from the ice chest during transportation from the field to the laboratory.

Travel Blanks and Field Duplicates

Potential field contamination was assessed through analysis of travel blanks and duplicate grab samples. Field travel blanks were collected for each monitoring station during every sampling event to quantify post sampling contamination. The monitoring program also included field duplicates to assess the precision of laboratory results. A field duplicate, the origin of which was unknown to the laboratory, was collected for each sampling event. This methodology for assessing post sampling contamination and laboratory testing procedures provided data to measure the precision and accuracy of the laboratory results.

3.3 LABORATORY ANALYSES

The Department of Agricultural Commissioner/Weights and Measures (ACWM) Environmental Toxicology Laboratory provides water quality laboratory and related services to the LACDPW. The ACWM lab is state certified to perform the water quality analyses contracted by LACDPW. The ACWM Lab maintains a laboratory analysis program that includes Quality Assurance and Quality Control protocols consistent with the objectives of the monitoring program required by the Permit.

3.3.1 Chemical and Biological Analysis

The suite of analyses and associated minimum levels (MLs) for samples collected at mass emission stations are specified in the Municipal Storm Water Permit. All the laboratory methods used for analysis of the storm water samples are approved by the California Department of Health Services and are in conformance with U.S. Environmental Protection Agency (USEPA) approved methods.

Table 3-1 shows all the constituents monitored during the 2002-2003 reporting period, including constituents analyzed with composite or grab samples. The table lists the method number, the PQL (which is the same as ML as defined in the Municipal Storm Water Permit), the method detection limit (MDL), and other relevant information for each constituent.

The Municipal Storm Water Permit defines MDL and ML (i.e. PQL) as follows:

MDL means the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. ML means the concentration at which the entire analytical system must give a recognizable signal and acceptable calibration point. The ML is the concentration in a sample that is equivalent to the concentration of the lowest calibration standard analyzed by a specific analytical procedure, assuming that all the method specified sample weights, volumes, and processing steps have been followed. Throughout this report, "0" for sample results indicates the analyte concentration is less than the ML.

The primary objective of the laboratory QA/QC program is to ensure that the analyses are scientifically valid, defensible, and of known precision and accuracy. The ACWM laboratory maintains QA/QC procedures (as described in their Quality Assurance Manual) in accordance with requirements of the California Department of Health Services. The ACWM laboratory standard operation procedures include method validation, equipment calibration, preventive maintenance, data validation procedures, assessment of accuracy and precision, corrective actions, and performance and system audits. ACWM Lab conducted the QA/QC review and data validation for the 2002-2003 monitoring data, and the QA/QC documentation is available within

the ACWM Lab files. The validated data as provided by the ACWM Lab were used for data analysis and interpretation with no further QA/QC review.

3.3.2 Toxicity Analysis

The samples were subjected to the Ceriodaphnia dubia 7-day survival and reproduction tests in addition to the Strongylocentrotus purpuratus (sea urchin) fertilization test as a measure of toxicity. Performed as multi-concentration tests, sample concentrations of 100%, 56%, 32%, 18%, 10% and 0% (N-control) were used to determine the level of toxicity. These tests were conducted under guidelines prescribed in *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms* (US EPA, 1995).

Water quality measurements (temperature, pH, dissolved oxygen, hardness, conductivity, and alkalinity) were made for each sample at the beginning and throughout each test. These measurements were performed to ensure there were no large variations in water quality, which can affect the accuracy of the toxicity tests.